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GAS-GENERATING PYROTECHNICAL COMPOSITIONS AND
PYROTECHNICAL COMPOUNDS FOR AUTOMOTIVE SAFETY

The present invention relates to pyrotechnic gas generation, in particular to inflate airbags used in systems for protecting the occupants of a motor vehicle. More particularly, the invention relates to pyrotechnic compositions generating, at temperatures which are acceptable to automotive safety, clean gases termed "cold" gases which are rich in nitrogen and are non-toxic, and it also relates to pyrotechnic compounds able to be obtained from such compositions.

For various pyrotechnic requirements, in particular to ensure the correct inflation of airbags, pyrotechnic gas generators must, over extremely short periods of the order of thirty milliseconds, provide clean gases, *i.e.* which are free of solid particles which could constitute hot spots and which might damage the airbag wall, and which are non-toxic, *i.e.* containing small quantities of oxides of nitrogen, oxides of carbon and chlorinated products.

United States patent US-A-5 608 183 discloses pyrotechnic gas-generating compositions comprising a reducing charge constituted by guanidine nitrate (GN) and an oxidizing charge constituted by basic copper nitrate (BCN) in predetermined proportions. Such compositions are very advantageous since they burn at low temperatures, less than 2000 K, allowing them to be used in gas generators for airbags, and since they can produce high gas yields during combustion thereof.

However, as described, for example, in US-A-6 143 102, such compositions have low combustion rates, in particular due to the presence of guanidine nitrate in the composition (see also column 3 of US-A-6 550 808). Further, it has been noted that such compositions are difficult to ignite and they have very low combustion temperatures, which greatly reduces their inflation power ("inflation power" is defined as the product of the gas yield on combustion multiplied by its combustion temperature). When used in the automotive safety field to inflate an airbag, the combustion temperature of the composition must remain low, if possible below 2200 K. In fact, at temperatures of less than 2200 K, it is still possible to use airbags with an inner wall which is uncoated. From a cost viewpoint, this may prove to be decisive in a market which is as

competitive as the automobile market. However, too low a combustion temperature penalizes the inflation power of the composition excessively.

European patent applications EP-A-1 279 655 and EP-A-1 130 008 describe methods of producing gas-generating compounds. Long lists are provided of substances which may be suitable as constituents of those compounds, as the reducing charge, as the oxidizing charge, and as additives. The production of small-diameter mono-perforated monolithic compounds is described in general manner.

Thus, the invention aims to provide an extrudable pyrotechnic composition (which, in general, is suitable for preparing mono- or multi-perforated monolithic compounds) which is capable of generating clean, non-toxic gases at low temperatures of less than 2300 K, allowing it to be used to inflate an uncoated airbag, which ignites readily, and which has a satisfactory inflation power.

This aim is achieved by a pyrotechnic gas-generating composition comprising an oxidizing charge constituted by basic copper nitrate (BCN), a reducing charge constituted by guanidine nitrate (GN) and a binder, the composition being characterized in that it also comprises:

- an additional reducing charge selected from the group formed by hexogene (RDX), octogene (HMX), penthrite (PETN), triaminoguanidine nitrate (TAGN), nitroguanidine, 3-nitro-1,2,4-triazol-5-one (ONTA) and mono- and bi-tetrazoles; and/or, advantageously and

- an additional oxidizing charge which forms a solid solution obtained by substitution with guanidine nitrate (GN); and

in that the binder, which is hydrosoluble, is based on a mixture of at least one carboxymethylcellulose with a high molecular mass and at least one carboxymethylcellulose with a low molecular mass, in a mass ratio in the range 95/5 to 60/40.

According to the invention, basic copper nitrate (hereinafter BCN) with formula $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$, is selected as the oxidizer since it has the advantage of being perfectly stable and, combined with a reducing agent, of burning by forming copper residues that are easy to filter. Further, BCN is insoluble in water, which is advantageous when the composition uses a hydrosoluble binder which allows it to be fabricated by extrusion. BCN also has a satisfactory gas yield which is higher than that

of compounds such as copper oxide, and a relatively high oxygen balance (OB) of +30%.

In an advantageous implementation of the invention, the basic copper nitrate (BCN) is present in a mass fraction in the range 40% to 60% (highly advantageously in the range 50% to 60%) of the total composition mass.

According to the invention, the selected reducing charge is guanidine nitrate (GN). Guanidine nitrate (GN) is an organic compound which is rich in nitrogen, stable, and inexpensive. Guanidine nitrate (GN) has good ageing properties, as measured by the 400 hour test at 107°C. Further, the presence of guanidine nitrate (GN) in the composition improves the gas yield of the composition. Guanidine nitrate (GN) has a negative enthalpy of formation, also having the effect of reducing the combustion temperature of the composition.

In an advantageous embodiment of the invention, the guanidine nitrate (GN) is present in a mass fraction in the range 20% to 55% (highly advantageously in the range 20% to 40%) of the total composition mass.

The presence of the additional reducing charge in the composition of the invention notably allows to improve the gas yield and to facilitate ignition of said composition, thus rendering it more reliable, and avoiding the need for an ignition charge. Ignition charges are expensive; thus, using a composition of the invention can reduce the cost of the gas generator.

In a preferred embodiment, the selected additional reducing charge is hexogene (RDX) or octogene (HMX).

Said additional reducing charge, when present, is generally present in a mass fraction of less than 15% with respect to the total composition mass.

The presence of a specific additional oxidizing charge in the composition of the invention can in particular:

- improve the gas yield;
- facilitate ignition of said composition; and also
- improve the combustion rate of said composition.

It also facilitates implementation of the method of producing said composition, and of producing compounds from said composition.

The additional oxidizing charge able to be used is thus not any oxidizing charge. It is selected for forming a solid solution obtained by substitution with the guanidine nitrate (GN).

5 This type of solid solution resulting from substitution (eutectic) is known *per se* to the skilled person. The chemical substances in question (in the present case guanidine nitrate and the second oxidizer) must have:

- a similar molecular size;
- the same type of crystal lattice; and
- the same valency (or oxidation number).

10 Entirely surprisingly, the inventors have discovered the great importance of this type of solution in the context of the invention. The impact on the combustion rate is considerable.

15 Amongst the numerous known oxidizers already used in the pyrotechnics field, only those which form a solid solution obtained by substitution with guanidine nitrate are suitable for use in compositions of the invention. In particular, ammonium perchlorate, potassium perchlorate, ammonium nitrate, sodium nitrate, and potassium nitrate are suitable. Ammonium perchlorate and potassium perchlorate are particularly suitable. The use of ammonium perchlorate is particularly recommended. These particular oxidizers are dealt with below.

20 In general, said additional oxidizing charge, when present, is present in a mass fraction of less than 10%, advantageously less than 10%, of the total composition mass.

25 Ammonium perchlorate is a very strong oxidizer and has a very good gas yield. Its highly oxidizing nature allows the proportion of reducing charge, and thus of guanidine nitrate (GN) in the composition, to be increased, GN also having a very good gas yield. Like the additional reducing charge, the presence of ammonium perchlorate in the composition can facilitate ignition of the composition. In the automotive safety field, almost all of the pyrotechnic composition must burn at a pressure of the order of 20 MPa [megapascals] in 30 ms [milliseconds] to 40 ms for use in a passenger or driver airbag, or in 20 ms in a side airbag. These combustion times must be adhered to in a composition intended for automotive safety. When present, ammonium perchlorate acts as a
35 "booster" in the composition.

Further, when the pyrotechnic product obtained burns in parallel layers, the combustion rate V_c satisfies the following law:

$$V_c = a \cdot p^n$$

in which a is a constant and n the pressure exponent. Combustion of a pyrotechnic compound is above all a chemical reaction and is thus temperature-dependent. Using ammonium perchlorate can reduce the pressure exponent, which renders the composition less dependent on pressure and thus less temperature-dependent. In the present invention, the pressure exponent is particularly low, considerably less than 0.7, which means that the pyrotechnic compound can be caused to function at temperatures in the range -35°C to 85°C . The composition of the invention may thus be used in an automotive vehicle.

Even though ammonium perchlorate or potassium perchlorate is a strong oxidizer and has advantageous combustion properties, its use in a composition leads to the production of high combustion temperatures and to the generation of combustion gases which can contain a fairly high level of hydrogen chloride. To avoid these problems, it is highly recommended that these oxidizers be used in small amounts, generally less than 10%, preferably less than 10% (of the composition mass). An indication of these maximum values of 15% or 10% has already been given in a general manner with reference to the use of any suitable additional oxidizer.

The composition of the invention is also capable of including a transition metal oxide to catalyze decomposition of the additional oxidizer. Said transition metal oxide may in particular be an oxide of iron, copper, or manganese, generally present in an amount of less than 5% by weight.

It is stated above that compositions of the invention include an additional reducing charge as described above and/or an additional oxidizing charge as described above. Advantageously, they include said additional reducing charge and said additional oxidizing charge.

Thus, they are advantageously of the type including:

- basic copper nitrate (BCN) and an additional oxidizing charge; and
- guanidine nitrate (GN) and an additional reducing charge.

Said specific oxidizer(s) and reducer(s) are, in a characteristic manner, included in a specific hydrosoluble binder. Said specific hydrosoluble binder is advantageous:

· in that it is hydrosoluble. (Some patent applications, such as
5 French patent application FR-A-2 772 370, describe the use of a cross-linked reducing binder based on silicone resin or based on epoxy resin. The binder is present in that composition in an amount which is advantageously in the range 6% to 10% of the total composition weight. To be suitable for production by extrusion with a twin-screw extruder, a
10 composition must have a binder content of the order of 4% or 5%, for example of the total composition mass and necessitates the use of a solvent for the binder. The binders used in that prior art composition require the use of organic or halogenated solvents. However, the use of halogenated solvents such as trichloroethylene is regulated, which greatly
15 complicates the manufacture of such a composition and increases its manufacturing cost. Similarly, the use of organic solvents such as ketone type solvents (acetone, methylethylketone, etc, for example) requires the use of complex solutions to control the emissions of volatile organic compounds (VOC). The hydrosoluble binder in the compositions of the
20 invention avoids having to use such organic or halogenated solvents during granulation or extrusion steps involved pyrotechnic compounds); and

· in that it is based on a mixture of at least one carboxymethylcellulose with a high molecular mass and at least one
25 carboxymethylcellulose with a low molecular mass in a mass ratio in the range 95/5 to 60/40; *i.e.* in that it includes long fibers and short fibers, in the ratio indicated above.

The notions of high and low molecular masses are defined below. Clearly, they refer to mean molecular masses. The term "high molecular
30 mass" as used in the present application and claims means a mean molecular mass of more than 250,000 g/mol [grams/mol], advantageously 700,000 g/mol or more. The term "low molecular mass" as used in the present application and claims means a mean molecular mass of less than 100,000 g/mol, generally much less than 90,000 g/mol. These definitions
35 will come as no surprise to the skilled person.

Carboxymethylcellulose performs well since it has:

- good ageing behavior, in particular as measured in an ageing test carried out for 400 hours at 107°C; and

- an advantageous oxygen balance. Compositions used in the automotive safety field must have an equilibrated oxygen balance (OB). By definition, a composition is termed "equilibrated" in oxygen when the composition comprises sufficient oxygen so that after reaction, the various compounds of the composition are in the form of CO₂, H₂O and N₂. The oxygen balance of the binder must be as low as possible. Carboxymethylcellulose has a much higher oxygen balance than the oxygen balance of elastomeric type binders.

Carboxymethylcellulose, a mixture of short and long fibers as defined above, performs particularly well in operations of granulation, compression, and extrusion, and is entirely suitable for processing the composition into the form of pellets, disks, or monolithic blocks, which are mono- or even multi-perforated. The mixture of short and long fibers can produce:

- in solution, in a minimum of water, a continuously pumpable and meterable gel, accepting a large amount of solid charge; and
- an extruded product which does not deform under its own weight.

The specific hydrosoluble binder as defined above is generally present in compositions of the invention in a mass fraction in the range 2% to 15% of the total composition mass. Beyond 15%, its influence may be deleterious to the oxygen balance of the composition.

The specificity of the binder for the compositions of the invention means that compounds can be obtained by continuous extrusion using a continuous twin-screw type extruder, which compounds have a configuration described in the profession as a monolithic block (or grain) with one or multiple perforations, with an external diameter of a few millimeters to about twenty millimeters. The number of perforations may vary from 1 to 19 for perforations 0.5 mm [millimeters] to 1.5 mm in diameter.

The composition of the invention may also include additives, in particular additives acting as catalysts for combustion or agents for trapping solid particles produced during combustion. Said agents can trap

solid particles produced during combustion to create residues which are of a sufficient size to allow them to be filtered. Additives which are well known in the field of compositions for automotive safety, for example alumina or silica, may be added to the composition of the invention.

5 In a second aspect, the present invention provides compounds which are able to be obtained from the pyrotechnic compositions described above.

 In a first variation, pyrotechnic compounds having a composition as described above are manufactured and shaped by a pelletization or disk
10 compression process.

 In a second variation, pyrotechnic compounds having a composition as described above are manufactured and shaped by an extrusion process.

 In the invention, pyrotechnic compounds having a composition of
15 the invention can be mass produced by disk compression or pelletization.

 Before the pelletization operation, a step of preparing a powder must be carried out. This step is not simply a matter of mixing the various dry constituents. To carry out the pelletization operation, it is necessary to obtain a powder that flows properly. This preparation step is a granulation
20 operation consisting in starting from the various materials constituting the composition of the invention in powder form to make grains of larger grain size, of the order of a few hundred microns. Once this powder has been obtained, the pelletization operation can be carried out.

 These pelletization or compression processes *per se* are known to
25 the skilled person.

 In the invention, pyrotechnic compounds having a composition of the invention may also be obtained by extrusion. Extrusion is rendered possible, is indeed optimized by the presence of carboxymethylcellulose with added water. Assuming that ammonium perchlorate or potassium
30 perchlorate is used, a small quantity of water should be incorporated to prevent said perchlorate from dissolving. The method of producing pyrotechnic compounds by extrusion advantageously comprises a step for continuously supplying a mixing and extrusion apparatus such as a twin-screw extruder with, on the one hand, the oxidizing charge(s) (BCN and
35 the optional additional oxidizing charge) and with, on the other hand, the

reducing charge(s) (GN and the optional additional reducing charge) pre-mixed with the binder used (the specific binder used). After mixing, using the extruder, a section rod is extruded which is oven-hardened, and then cut to the desired length, for example into the form of granulates. Cutting
5 may also be carried out, in certain cases in which dimensional requirements are not so severe, before oven hardening. The monolithic compounds obtained may be mono- or multi-perforated. The specificity of the binder (mixture of short and long fibers) allows the compounds to be obtained in the multi-perforated form.

10

Table 1 below shows a few examples of the formulations for the compositions of the invention. The percentages indicated are percentages by weight.

TABLE 1

Ex**	C*	CMC-Na	BCN	GN	RDX	HMX	ONTA	O.M.	NH ₄ ClO ₄	NaNO ₃	KClO ₄
Ref		3.6	52.4	41				3			
1		8	59.6	22.4		10					
2		3.6	43.1	42.7				3	7.6		
3		2	53.4	39.6	5						
4		2	52.4	30.6	15						
5		4	50.8	30.2	10				5		
6		4	54.1	38.9					3		
7		8	60.3	21.7			10				
8		4	52	34	5					5	
9		4	58.9	27.1	10						
10		2	46.2	36.8	12.3			2.7			
11		4	42	43.9				2.7	4.3	3.1	

C* : constituents

Ex** : examples

The following abbreviations were used in this table:

5	CMC-Na	= sodium carboxymethylcellulose (quantity expressed as a percentage). The binder used was a mixture of CMC-Na with a high mean molecular mass: $M_w \approx 700,000$ g/mol (BLANOSE [®] from AQUALON HERCULES - grade 7H -) and CMC-Na with a low mean molecular mass: $M_w \ll 90000$ g/mol (BLANOSE [®] from AQUALON HERCULES - grade 12UL -). The mixtures in question were generally 85/15 mixtures (mass ratio: high molecular mass CMC-Na/low molecular mass CMC-Na).
10	BCN	= basic copper nitrate (quantity expressed as a percentage)
	GN	= guanidine nitrate (quantity expressed as a percentage)
	RDX	= hexogene (quantity expressed as a percentage)
	HMX	= octogene (quantity expressed as a percentage)
15	ONTA	= 3-nitro-1,2,4-triazol-5-one (quantity expressed as a percentage)
	O.M.	= metallic oxide (quantity expressed as a percentage) such as SiO_2 or Al_2O_3 , used as a ballistic catalyst and/or particle trapping agent.

20

For the compositions of Table 1 above, the theoretical results shown in Table 2 below are obtained.

TABLE 2

Ex	O.B. (%)	Yield (mol/100g)	Tc (K)
Ref	-2.2	2.65	1819
1	-2	2.43	2031
2	-2.2	2.85	2001
3	-1	2.70	1962
4	-1	2.65	2205
5	-0.5	2.65	2156
6	-0.5	2.65	1873
7	-2	2.38	1920
8	+0.5	2.52	1959
9	+0.5	2.44	1987
10	-3.5	2.80	2178
11	-3	2.84	1959

O.B. = oxygen balance (as a percentage)

Yield = gas yield (as moles per kg of burned composition)

Tc = combustion temperature (K).

5

Table 2 above shows that by adjusting the equivalent oxygen balance (OB), the proposed novel formulations allow an increase in the gas yield and/or the combustion temperature, which results in a larger gas volume obtained for the same mass of propergol. Similarly, as these examples show, it is also possible to adjust the OB of said compositions to adapt it to the requirements of each application. The good performance of said compositions is confirmed by the results in the manometric chamber (Table 4 below).

15

Table 3 below shows the results obtained for firing 30 g [grams] of a composition in accordance with the various examples of Table 1 into a 60 L [liter] tank.

TABLE 3

Ex	Tall18 (ms)	Tt 0.9 (ms)	P _{max tank} (MPa)
Ref	3.1	46	0.18
2	2.5	38	0.21
4	2.4	40	0.23

Tall18 = time to reach a pressure of 18 MPa in the generator chamber used for the tests;

5 Tt0.9 = time between firing and the time at which the tank pressure is 90% of the maximum pressure in the tank.

The results shown in Table 4 below were obtained when firing in the manometric tank:

10 **TABLE 4**

Ex	V _c (20 MPa) mm/s	Pressure exponent
Ref	14.2	0.5 (11-24 MPa)
2	22	0.7 (16-37 MPa)
10	18	0.3 (15-35 MPa)
11	22	1 (15-35 MPa)

V_c = combustion rate.

15 In the above reference example, the composition was ignited with 140 mg [milligrams] of TiPP powder (powder based on titanium and potassium perchlorate) and with 450 mg of ignition charge. In contrast, for the compositions of Examples 2, 10 and 11, ignition was carried out with only 140 mg of TiPP. This shows that the presence of ammonium perchlorate or RDX in the compositions can greatly improve ignition and means that ignition charge can be dispensed with.